

Catalytic steam reforming of model biogas

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Abstract

Catalytic steam reforming of a model biogas ($\text{CH}_4/\text{CO}_2 = 60/40$) is investigated to produce H_2 -rich synthesis gas. Gas engines benefit from synthesis gas fuel in terms of higher efficiency and lower NO_x production when compared to raw biogas or CH_4 . The process is realized in a fixed bed reactor with a Ni-based catalyst on $\text{CaO}/\text{Al}_2\text{O}_3$ support. To optimize the performance, the reactor temperature and the amount of excess steam are varied. The experimental results are compared to the theoretical values from thermodynamic calculation and the main trends of CH_4 conversion and H_2 yield are analyzed and verified. Finally, optimal reactor temperature is pointed out and a range of potential steam to methane ratios is presented. The experimental results will be applied to design a steam reformer at an existing anaerobic biomass fermentation plant in Strem, Austria.

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1. Introduction

Since most of the global warming is likely to result from emission of CO_2 , the reduction of greenhouse gas emission is being debated in recent years [1]. The sustainable use of biomass for energy production does not contribute to CO_2 emission and has therefore a high potential to reduce them.

Anaerobic digestion of biomass is one way of producing a gaseous fuel (biogas) from renewable sources. Biogas has a typical composition of 55–70 vol% CH_4 , 27–44 vol% CO_2 , <1 vol% H_2 and <3 vol% H_2S as well as traces of NH_3 . Today, it is mainly combusted in gas engines or supplied to a gas distribution system after the separation of unwanted substances [2].

It has been shown by Herdin et al. [3] and Gruber et al. [4] that, in comparison to CH_4 , gas engines fuelled with H_2 -rich gases have higher efficiency and lower nitrogen oxide emissions. This also applies for a high CO content but the effect is somewhat smaller [3]. Therefore, the reforming of biogas before the combustion in gas engines seems to be

a profitable process. The efficiency benefits from H_2 -rich fuels are shown in Fig. 1. The increase of the efficiency is up to 2–3% if pure H_2 , instead of CH_4 , is used as gas engine fuel. If syngas fuel is used the values are somewhere between H_2 and CH_4 .

Steam reforming of CH_4 produces a H_2 - and CO -rich gas. Since CO also contributes to performance improvements in gas engines, the usually following shift reactor can be omitted. This way the process is kept simple and additional investment costs are avoided.

Fig. 2 shows the lean limits and NO_x production of different gas engine fuels. Even though the NO_x production is very high at air/fuel ratio near 1, it is possible to run the gas engine on very low NO_x production when increasing the air/fuel ratio. This generally applies to all tested fuels but because of the very high lean limit, best results are achieved with H_2 [3,4].

To demonstrate the low NO_x production and higher engine efficiency under real fermenter conditions, it is intended to erect a steam reformer at an existing anaerobic biomass fermentation plant in Strem, Austria (see Table 1 for fermenter details). A great number of experiments on steam reforming of methane has been performed by different authors, but there is not much literature concerning

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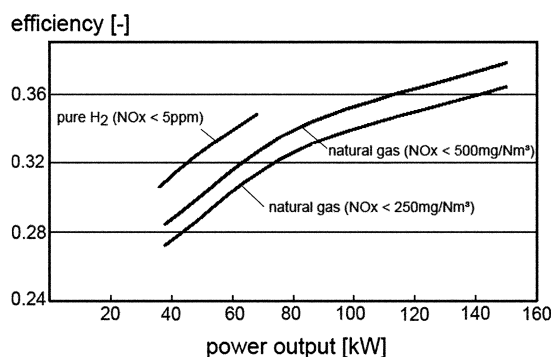


Fig. 1. Gas engine efficiency on fuel variation [3].

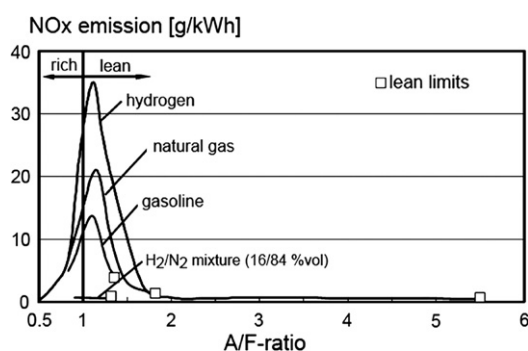


Fig. 2. Lean limit and NO_x production of different fuels [3,4].

Table 1
Overview of the anaerobic biomass digestion plant in Strem, Austria

Feeded biomass	Grass, clover, corn
Power (electr.) (kW)	526
Power (heat) (kW)	600
Gas production (m ³ _N /h)	≈275
LHV (MJ/m ³ _N)	17.9
Biogas composition (after biological desulphurization)	
CH ₄ (vol%)	49.9
CO ₂ (vol%)	42.7
H ₂ O (vol%)	4.8
N ₂ (vol%)	2.1
O ₂ (vol%)	0.5
H ₂ S (ppm)	50–100

The O₂ and N₂ content result from desulphurization with air. The biogas composition varies with feeded biomass.

steam reforming of biogas (combined steam and dry reforming process) available. Therefore, experiments on laboratory scale are performed prior to the erection of the pilot steam reformer in Strem. For this application it is very important to find optimal values for reactor temperature and amount of excess steam to ensure proper reforming at minimal energy forfeit. Furthermore, the gas engine produces a lot of waste heat which is currently not used. This energy could be integrated in the process to optimize the system. Since the benefits of syngas fuel for gas engines already apply at low H₂ and CO concentrations [3,4], only a side stream of biogas will be reformed and then mixed with the remaining raw biogas. Therefore, there are a lot

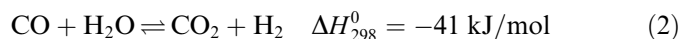
of parameters to be varied to find an optimum overall process design.

For steam reforming of biogas a Ni-based catalyst on CaO/Al₂O₃ support is used. These catalysts have high activity for steam reforming and dry reforming processes at low costs and are thus applied in many industrial steam reforming applications [5–7]. Much research has been performed on Ni-based catalysts and therefore, coking and deactivation are well understood [8–11]. For all these reasons, a Ni-based catalyst seems to be a promising choice. In Strem, H₂S is removed down to 50–100 ppm by biological desulphurization with air. Since already very small concentrations of H₂S in the feed gas lead to catalyst deactivation [10], the traces of H₂S will be removed with an activated carbon filter, impregnated with copper and chrome. In commercial applications, the activated carbon filter will probably be replaced by other technologies. NH₃ is not detected in the raw biogas in Strem but would also have little effect on catalyst activity [12].

The reforming of hydrocarbons is basically described by the steam reforming and the dry reforming of CH₄ [5,7,8,12–20]. The associated reactions are the steam reforming reaction



the water gas shift reaction



and the dry reforming reaction with CO₂



which plays a minor role when enough H₂O is available. Even though the dry reforming reaction tends to coke formation, it can already be avoided when small amounts of H₂O are added [15]. Therefore, the resulting syngas consists of unreacted CH₄, CO₂, CO, H₂ and excess H₂O. When applying high ratios of H₂O to CH₄ and high reactor temperatures the equilibrium concentration of methane is negligible. The excess H₂O can be removed by condensation.

It has been shown by Effendi et al. [12] and Zhang et al. [13] that the steam reforming process also works for a model biogas (high CH₄ and CO₂ content). It is assumed though that, due to the high content of CO₂, the dry reforming reaction will play a major role in the overall reaction. According to different authors [12–14], steam reforming of biogas can be performed in fixed and fluidized bed reactors. Here a fixed bed reactor design is used to keep the apparatus simple and cheap.

In large scale H₂ production plants the steam reformer is operated at high temperatures (900–1000 °C) due to the strong endothermic character of the reforming reaction (see Eq. (1)), while the shift reactor(s) run at low temperatures (150–400 °C) to maximize the H₂ output. This second step is omitted in this application since CO also contributes to low NO_x production and efficiency increase of the gas

engine (see above) and again, to keep the installations simple and cheap.

2. Experimental

The major reactor dimensions and operating parameters are pointed out in Table 2. CH₄ and CO₂ are continually mixed with demineralized H₂O in liquid state before entering the reactor. In an electrical heater the water is evaporated and the gas mixture is superheated to reactor temperature. The superheater pipe consists of a high number of elbows to ensure uniform gas distribution in the reactor. The feed gas then enters the fixed bed catalyst reactor, which is also heated to cover the energy demand of the endothermic reactions taking place. Along the reactor height and after the catalyst bed, thermocouples are installed for temperature measurement and control. The reformed gas is then cooled in a 2-stage cooler down to approximately 2 °C and the condensing excess water is removed in a water trap. For gas analysis a gas chromatograph (CO, CO₂, CH₄) and a flame ionization analyzer (CO, CO₂) are used. H₂ is not directly measured but can be calculated from mass balance since it is the only unknown concentration. Besides, the H₂ content is spot-checked with a multi component gas analyzer. Additional data of used gas analyzers is shown in Table 3. The necessary H₂O is fed to the biogas with a calibrated peristaltic pump. The ratio of H₂O to CH₄ is calculated from the storage tank mass difference during the experiments.

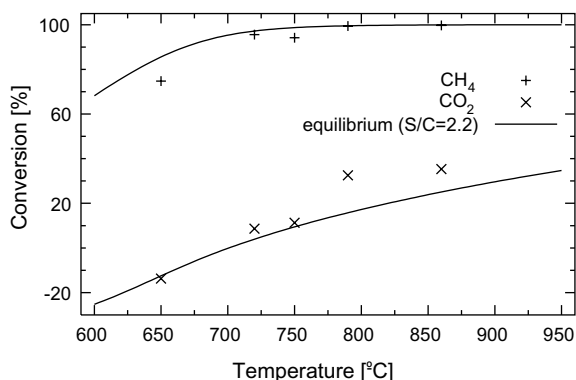


Fig. 3. CH₄ and CO₂ conversion at $S/C \approx 2.2$ as a function of the temperature.

Table 2
Major dimensions and operating parameters of the laboratory scale steam reformer

Inner diameter	mm	47
Catalyst input	g	240–360
Model biogas flow	l _N /min	4.6–8.0
Reactor temperature	°C	650–860
Residence time	s	≈0.5
Space velocity	m ³ /(kg·h)	≈11.0
Reactor wall material		1.4841 X15CrNiSi25-20

Table 3
Types and statistical errors of the used gas analyzers

Gas analyzer	Measured species	Statistical error (%)
Syntech Spectras GC955	CH ₄ , CO ₂ , CO	1.0% abs
Rosemount type MLT3	CO ₂ , CO	1.0% abs
Rosemount type MLT4	H ₂	5.0% rel

Table 4
Physicals properties and chemical composition of the catalyst

Producer	Johnson Matthey Catalysts
Name	KATALCO 57-4
Form	4-hole cylinder
Diameter	14 mm
Length	19 mm
S_{BET}	12 m ² /g
Composition	
NiO	18 wt%
SiO ₂	<0.1 wt%
SO ₃	<0.05 wt%
Support	CaO/Al ₂ O ₃

The fixed bed reactor is filled with an industrial steam reforming catalyst on Ni basis (see Table 4 for details). The amount of catalyst, and therefore the bed height, is varied. Since the space velocity (see definition (5)) is kept constant throughout all experiments, the amount of biogas to be reformed has to be changed when varying the reactor temperature. This implies a change of heating power as well. A second method to maintain the designated space velocity is changing the amount of catalyst. This is done in cases where the maximum heating power is exceeded.

Before each experiment, the catalyst is replaced with new particles to ensure constant reactor properties throughout the series of experiments. At start up, the reactor is streamed with hot nitrogen to avoid temperature differences between the catalyst particles. Once the reactor has reached the designated reaction temperature, the necessary amount of water is dosed to the nitrogen stream for approximately 10 min. Afterwards, the biogas is introduced into the reactor and nitrogen is disconnected from the system. Each experiment runs for approximately 8 h. Including preparation, start up (3 h) and shut down (2 h), each experiment lasts for approximately 14 h.

For all experiments a model biogas, consisting of 60 vol% CH₄ and 40 vol% CO₂, is used. This composition corresponds approximately to mean values of the biomass fermentation plant in Strem (dry, O₂ and N₂ free) for different sorts of feeded biomass. H₂S is not present since it will be removed at the pilot plant in Strem.

In a first set of experiments the reactor temperature is varied in a range of 650–860 °C at a constant steam to methane ratio $S/C = 2.2$.

$$S/C = \frac{\dot{N}_{H_2O}}{\dot{N}_{CH_4}} \left[\frac{\text{mol}}{\text{mol}} \right] \quad (4)$$

After an optimal reactor temperature is found, S/C is varied in the range of 1.7–4.5. All experiments are done at constant space velocity ($SV \approx 11.0 \text{ m}^3/\text{h} \cdot \text{kg}$).

$$SV = \frac{\dot{V}_{\text{Gas}}}{m_{\text{Kat}}} \left[\frac{\text{m}^3}{\text{h} \cdot \text{kg}} \right] \quad (5)$$

3. Results and discussion

To compare the results, a set of values is calculated from the measured gas compositions of the model biogas (BG) and the synthesis gas (SG). These are the conversion of CH_4

$$X_{\text{CH}_4} = \frac{\dot{N}_{\text{CH}_4, \text{BG}} - \dot{N}_{\text{CH}_4, \text{SG}}}{\dot{N}_{\text{CH}_4, \text{BG}}} = 1 - \frac{y_{\text{CH}_4, \text{SG}}}{y_{\text{CH}_4, \text{BG}} \cdot y_{\text{Carbon}}} [-], \quad (6)$$

the conversion of CO_2

$$X_{\text{CO}_2} = \frac{\dot{N}_{\text{CO}_2, \text{BG}} - \dot{N}_{\text{CO}_2, \text{SG}}}{\dot{N}_{\text{CO}_2, \text{BG}}} = 1 - \frac{y_{\text{CO}_2, \text{SG}}}{y_{\text{CO}_2, \text{BG}} \cdot y_{\text{Carbon}}} [-], \quad (7)$$

and the H_2 yield

$$Y_{\text{H}_2} = 0.25 \cdot \frac{\dot{N}_{\text{H}_2, \text{SG}}}{\dot{N}_{\text{CH}_4, \text{BG}}} = 0.25 \cdot \frac{y_{\text{H}_2, \text{SG}}}{y_{\text{CH}_4, \text{BG}} \cdot y_{\text{Carbon}}} [-], \quad (8)$$

with the concentration of carbon containing species

$$y_{\text{Carbon}} = y_{\text{CH}_4, \text{SG}} + y_{\text{CO}_2, \text{SG}} + y_{\text{CO}, \text{SG}} [-]. \quad (9)$$

3.1. Variation of the reactor temperature

In this set of experiments S/C is kept constant at various reactor temperatures. Since the used peristaltic pump has some deviations in the supplied water flow, S/C varies in the range of 2.15–2.24. In one case, S/C even reaches 2.76. This data point can hardly be compared to the others but is still included in resulting plots. The equilibrium is plotted for the mean value of the variations which is at $S/C = 2.2$.

Fig. 3 shows the CH_4 and CO_2 conversion as a function of the reactor temperature. Increasing the reactor temperature implies a steep increase of CH_4 conversion until 750°C

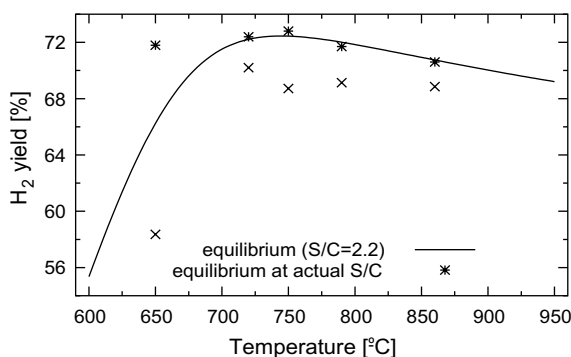


Fig. 4. H_2 yield at $S/C \approx 2.2$ and actual operation conditions as a function of the temperature.

is reached. Above 750°C the gain in conversion is very low. Therefore the reactor temperature should be within the range of 700 – 750°C but not below 700°C because from there the CH_4 conversion decreases significantly. The increase of CO_2 conversion with temperature shows that the dry reforming reaction with CO_2 takes place. At higher temperatures, this reaction is favored and therefore CO_2 is consumed.

As seen in Fig. 4, the H_2 yield has a maximum somewhere within the range of 700 – 800°C . At higher temperatures, the increase of H_2 production from the steam and dry reforming reaction (higher conversion) is lower than the decrease of H_2 production from the shift reaction (equilibrium is shifted towards CO and H_2O). This leads to a decrease of the H_2 content. The measured values follow this trend but the maximum is difficult to determine. In Fig. 4, the equilibrium state is plotted for $S/C = 2.2$ and for the actual S/C ratio during testing.

The syngas composition at the reactor outlet is plotted in Fig. 5. As seen in Fig. 4 a maximum of H_2 production should exist but it is very difficult to determine. At all reactor temperatures the syngas composition is constant throughout the experiments and catalyst deactivation is not observed in any case.

Considering these results, a reactor temperature of 750°C seems to be a promising choice. At this temperature the H_2 yield reaches its maximum and the CH_4 conversion

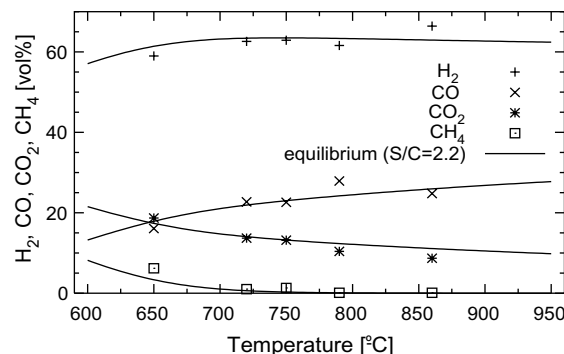


Fig. 5. H_2 , CO_2 , CO and CH_4 concentration in effluent at $S/C \approx 2.2$ as a function of temperature.

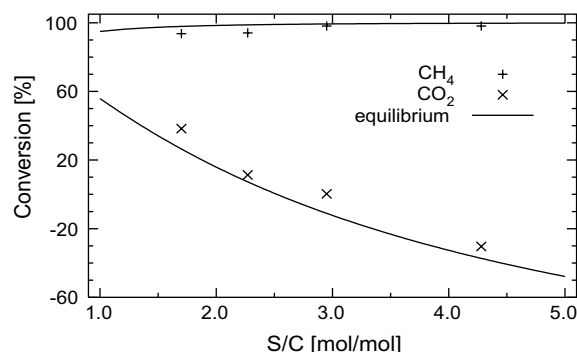


Fig. 6. CH_4 and CO_2 conversion at 750°C as a function of S/C .

is sufficiently high. In the next series of experiments the effect of S/C variation at a reactor temperature of 750 °C is investigated.

3.2. Variation of S/C

In a second series of experiments S/C is varied at a constant reactor temperature of 750 °C. Fig. 6 shows the conversions of CH_4 and CO_2 as a function of S/C . Increasing S/C in the feed gas results in a slight increase of CH_4 conversion. The CO_2 conversion, on the other hand, will decrease significantly. This means that the dry reforming reaction occurs rarely, compared to the steam reforming reaction. At $S/C \approx 2.9$ (thermodynamic prediction at $S/C \approx 2.6$), the conversion of CO_2 is zero. This means that above this value the overall reaction produces CO_2 – below this value the overall reaction is CO_2 consuming. Furthermore, an increase of S/C leads to a higher selectivity towards H_2 which results in an increased H_2 yield (see Figs. 7 and 8). S/C has a high impact on the H_2 output but also on the efficiency of the whole process, since the evaporation of water has a very high energy demand. Throughout the experiments, the syngas composition is constant at all ratios of S/C . Catalyst deactivation is not observed.

In all experiments the H_2 yield and CH_4 conversion do not reach equilibrium state. This has two possible reasons:

- (1) The space velocity in the reactor is too high for a complete reformation. This is not necessarily connected to bad performance. In the pilot plant application the synthesis gas will be mixed with raw biogas after the reformer. Therefore, the CH_4 concentration after the reformer does not necessarily have to be zero.
- (2) The fixed bed allows some of the model biogas to pass the reactor without proper contact with the catalyst. As seen in Tables 2 and 4 the ratio of inner reactor diameter to catalyst particle size is quite large. In the pilot plant this ratio will be much smaller and the effect should be minimized.

The space velocity also has a high impact on the investment costs of the installation. High space velocities induce small reactor dimensions and little catalyst content. At the same time, H_2 yield and CH_4 conversion are reduced. Therefore, the space velocity has a high potential for optimization.

As shown in Fig. 6, the CO_2 conversion follows the thermodynamic prediction quite well but all measured values are slightly above the equilibrium level. This phenomenon is explained by the difference of the CO_2 concentration to equilibrium state (see Fig. 8). Small differences in concentration have a high impact on the CO_2 conversion (see Eq. (7)).

Compared to the reactor temperature variation, there is no optimum value of S/C since both, the steam reforming and shift reaction, favor high H_2O partial pressures. The amount of excess steam will be limited with the available amount of waste heat. Therefore, this parameter has a high impact on the global efficiency of the process.

4. Conclusion

Steam reforming of a model biogas over a Ni-based catalyst is investigated in the present paper. It is shown that this is a promising process for producing a H_2 -rich synthesis gas. Depending on the steam to CH_4 ratio (S/C), the present CO_2 in the biogas is inert (high S/C) or acts as reaction partner for CH_4 (see dry reforming reaction (3)). The latter occurs at $S/C < 2.9$ (at 750 °C reactor temperature).

The reaction temperature has a high influence on CH_4 conversion and H_2 yield. While high temperatures lead to high CH_4 conversion, the H_2 yield reaches its maximum within the range of 700–800 °C at $S/C \approx 2.2$. Therefore, a reactor temperature of 750 °C is found to be the optimal choice.

An increase of S/C always goes along with an increase in CH_4 conversion and H_2 yield. However, the energy demand increases very rapidly because of the high energy demand to evaporate and superheat the excess water. On the basis of the investigated results, the pilot biogas steam reformer in Strem and future applications are being designed.

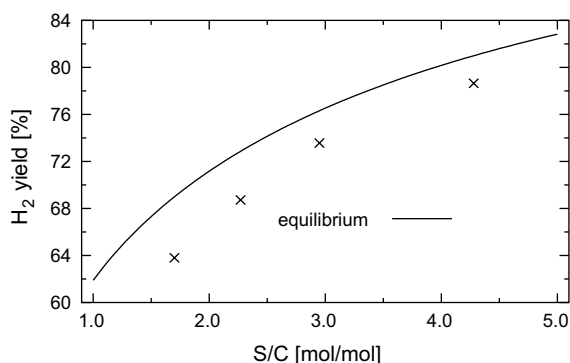


Fig. 7. H_2 yield at 750 °C as a function of S/C .

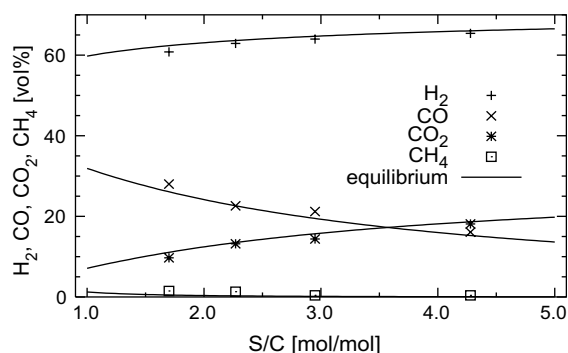


Fig. 8. H_2 , CO_2 , CO and CH_4 concentration in effluent at 750 °C as a function of S/C .

Catalyst deactivation is not observed at any testing conditions (syngas composition is constant throughout the experiments). Therefore it is concluded that deactivation is of minor importance at the applied duration of the experiments. Deactivation and coking will be of greater importance in the pilot plant in Strem where long term testing of the catalysts, regarding stability and coking, will be performed.

Acknowledgements

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References

- [1] Möllersten K, Yan J, Moreira JR. Potential market niches for biomass energy with CO₂ capture and storage – opportunities for energy supply with negative CO₂ emissions. *Biomass Bioenerg* 2003;25:273–85.
- [2] Kaltwasser B. Regenerative energieerzeugung durch anaerobe fermentation organischer Abfälle in biogasanlagen. 1st ed. Wiesbaden and Berlin: Bauverlag; 1980.
- [3] Herdin GR, Gruber F, Klausner J, Robitschko R, Plohberger D. Use of hydrogen and hydrogen mixtures in gas engines and potentials of NO_x emissions. In: ARES-ARICE symposium on gas fired reciprocating engines, Canada, 2005.
- [4] Gruber F, Herdin GR. The use of H₂-content process gas in gas engines. In: ASME international combustion engine division, spring technical conference, USA, 1997.
- [5] Tvigge MV. Catalyst handbook. 2nd ed. London: Manson Publ.; 1996.
- [6] Rostrup-Nielsen JR, Bak Hansen JH. CO₂-reforming of methane over transition metals. *J Catal* 1993;144:38–49.
- [7] Rostrup-Nielsen JR. Syngas in perspective. *Catal Today* 2002;71:243–7.
- [8] Fonseca A, Assaf EM. Production of the hydrogen by methane steam reforming over nickel catalysts prepared from hydrotalcite precursors. *J Power Sources* 2005;142:154–9.
- [9] Bengaard HS, Nørskov JK, Sehested J, Clausen BS, Nielsen LP, Molenbroek AM, et al. Steam reforming and graphite formation on Ni catalysts. *J Catal* 2002;209:365–84.
- [10] Rodríguez JC, Romeo E, Fierro JLG, Santamaría J, Monzón A. Deactivation by coking and poisoning of spinel-type Ni catalysts. *Catal Today* 1997;37:255–65.
- [11] Urasaki K, Sekine Y, Kawabe S, Kikuchi E, Matsukata M. Catalytic activities and coking of Ni/perovskites in steam reforming of methane. *Appl Catal A-Gen* 2005;286:23–9.
- [12] Effendi A, Hellgardt K, Zhang ZG, Yoshida T. Optimising H₂ production from model biogas via combined steam reforming and CO shift reactions. *Fuel* 2005;84:869–74.
- [13] Zhang ZG, Xu G, Chen X, Honda K, Yoshida T. Process development of hydrogenous gas production for PEFC from biogas. *Fuel Process Technol* 2004;85:1213–29.
- [14] Effendi A, Zhang ZG, Hellgardt K, Honda K, Yoshida T. Steam reforming of a clean model biogas over Ni/Al₂O₃ in fluidized- and fixed bed reactors. *Catal Today* 2002;77:181–9.
- [15] Li C, Fu Y, Bian G, Xie Y, Hu T, Zhang J. Effect of Steam in CO₂ Reforming of CH₄ over a Ni/CeO₂ – ZrO₂ – Al₂O₃ Catalyst. *Kinet Catal* 2004;45:679–83.
- [16] Chen X, Honda K, Zhang ZG. CO₂ – CH₄ reforming over NiO/ γ – Al₂O₃ in fixed/fluidized bed multi switching mode. *Appl Catal A-Gen* 2005;279:263–71.
- [17] Nurunnabi M, Li B, Kunimori K, Suzuki K, Fujimoto K, Tomishige K. Performance of NiO–MgO solid solution-supported Pt catalysts in oxidative steam reforming of methane. *Appl Catal A-Gen* 2005;292:272–80.
- [18] Souza MMVM, Aranda DAG, Schmal M. Reforming of methane with carbon dioxide over Pt/ZrO₂/Al₂O₃ catalysts. *J Catal* 2001;204:498–511.
- [19] Matsumura Y, Nakamori T. Steam reforming of methane over nickel catalysts at low reaction temperature. *Appl Catal A-Gen* 2004;258:107–14.
- [20] Rakass S, Oudghiri-Hassani H, Rowntree P, Abatzoglou N. Steam reforming of methane over unsupported nickel catalysts. *J Power Sources* 2006;158:485–96.